

UNCLASSIFIED

AD NUMBER

AD360916

CLASSIFICATION CHANGES

TO: **unclassified**

FROM: **confidential**

LIMITATION CHANGES

TO:

**Approved for public release, distribution  
unlimited**

FROM:

**Distribution authorized to DoD only;  
Administrative/Operational Use; MAY 1965.  
Other requests shall be referred to Office  
of Naval Research, 875 North Randolph St,  
Suite 1425, Arlington, VA 22203-1995.**

AUTHORITY

**31 May 1977, per document marking, DoDD  
5200.10.; st-a onr ltr 16 feb 1979**

THIS PAGE IS UNCLASSIFIED

**CONFIDENTIAL**

---

**AD 360916**

**DEFENSE DOCUMENTATION CENTER**

**FOR**  
**SCIENTIFIC AND TECHNICAL INFORMATION**  
**CAMERON STATION, ALEXANDRIA, VIRGINIA**



---

**CONFIDENTIAL**

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

NOTICE:

THIS DOCUMENT CONTAINS INFORMATION  
AFFECTING THE NATIONAL DEFENSE OF  
THE UNITED STATES WITHIN THE MEAN-  
ING OF THE ESPIONAGE LAWS, TITLE 18,  
U.S.C., SECTIONS 793 and 794. THE  
TRANSMISSION OR THE REVELATION OF  
ITS CONTENTS IN ANY MANNER TO AN  
UNAUTHORIZED PERSON IS PROHIBITED  
BY LAW.

---

CONFIDENTIAL

360916

360916

REPORT NO. 0235-01-22 (QUARTERLY)

PERIOD COVERED: 1 JANUARY - 31 MARCH 1965

CATALOGED BY: DDC  
AS AD NO.

RESEARCH IN FLUORO-NITRO  
COMPOUNDS (u)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

MAY 1965

COPY NO. CP 61-16

DDC

RESEARCH PROJECTS AGENCY

JUN 7 1965

CHEMICAL PRODUCTS DIVISION  
AEROJET-GENERAL CORPORATION  
AZUSA, CALIFORNIA

CONFIDENTIAL

(0235)

## NOTICE

REPRODUCTION IN WHOLE OR IN PART IS  
PERMITTED FOR ANY PURPOSE OF THE UNITED  
STATES GOVERNMENT.

## United States Patent Office Secrecy Order

### NOTICE

The Aerojet-General Corporation has filed patent applications in the U. S. Patent Office to cover inventions disclosed in this publication, and the Commissioner of Patents has issued a secrecy order thereon.

Compliance with the provisions of this secrecy order requires that those who receive a disclosure of the secret subject matter be informed of the existence of the secrecy order and of the penalties for the violation thereof.

The recipient of this report is accordingly advised that this publication includes information which is now under a secrecy order. It is requested that he notify all persons who will have access to this material of the secrecy order.

Each secrecy order provides that any person who has received a disclosure of the subject matter covered by the secrecy order is

"in nowise to publish or disclose the invention or any material information with respect thereto, including hitherto unpublished details of the subject matter of said application, in any way to any person not cognizant of the invention prior to the date of the order, including any employee of the principals, but to keep the same secret except by written permission first obtained of the Commissioner of Patents."

Although the original secrecy order forbids disclosure of the material to persons not cognizant of the invention prior to the date of the order, a supplemental permit attached to each order does permit such disclosure to:

"(a) Any officer or employee of any department, independent agency, or bureau of the Government of the United States.

"(b) Any person designated specifically by the head of any department, independent agency or bureau of the Government of the United States, or by his duly authorized subordinate, as a proper individual to receive the disclosure of the above indicated application for use in the prosecution of the war.

"The principals under the secrecy are further authorized to disclose the subject matter of this application to the minimum necessary number of persons of known loyalty and discretion, employed by or working with the principals or their licensees and whose duties involve cooperation in the development, manufacture or use of the subject matter by or for the Government of the United States, provided such persons are advised of the issuance of the secrecy order."

No other disclosures are authorized, without written permission from the Commissioner of Patents. Public Law No. 239, 77th Congress, provides that whoever shall "willfully publish or disclose or authorize or cause to be published or disclosed such invention, or any material information with respect thereto," which is under a secrecy order, "shall, upon conviction, be fined not more than \$10,000 or imprisoned for not more than two years or both." In addition, Public Law No. 700, 76th Congress, provides that the invention in a patent may be held abandoned, if it be established that there has been a disclosure in violation of the secrecy order.

It must be understood that the requirements of the secrecy order of the Commissioner of Patents are in addition to the usual security regulations which are in force with respect to activities of the Aerojet-General Corporation. The usual security regulations must still be observed notwithstanding anything set forth in the secrecy order of the Commissioner of Patents.

**CONFIDENTIAL**

May 1965

Report No. 0235-01-22  
(Quarterly)

## RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

K. Baum H. Nelson  
V. Grakauskas A. H. Remanick  
H. Marcus O. S. Schaeffler

### Analytical Support

C. L. Deuel  
K. Inouye

## A Report to

OFFICE OF NAVAL RESEARCH  
and  
ADVANCED RESEARCH PROJECTS AGENCY

Contract N0nr 2655(00)  
ARPA Order No. 170, Amendment No. 7  
Project Code 4910

Research reported in this publication was supported by the Advanced Research Projects Agency.

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, USC, Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

**GROUP 4**

Downgraded at 3-Year Intervals  
Declassified After 12 Years

### Von Karman Center

AEROJET-GENERAL CORPORATION

A Subsidiary of The General Tire & Rubber Company

**CONFIDENTIAL**

**CONFIDENTIAL**

Report No. 0235-01-22

**ABSTRACT**

The reactions of 1-difluoraminobutane and 2-difluoraminobutane with concentrated sulfuric acid gave the ions,  $\text{CH}_2=\text{NF}-\text{CH}_2\text{CH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}=\text{NFCH}_2\text{CH}_3$ , respectively: A 1:1 adduct of isoprene and difluoramine was obtained, using the boron trifluoride complex of phosphoric acid as catalyst. The reaction of 2,2-bis(difluoramino)octane with sulfuric acid, with vigorous agitation, gave 2-octanone. The reaction of  $\alpha,\alpha$ -dibromo- $\alpha$ -difluoraminotoluene with sodium 2-propenenitronate gave  $\alpha$ -bromo- $\alpha$ -fluoriminotoluene.

The fluorination of ethyl methoxycarbamate gave  $\text{N},\text{N}'$ -dimethoxy- $\text{N},\text{N}'$ -dicarbethoxyhydrazine instead of the expected NF derivatives.

Methyl  $\alpha$ -difluoraminobutyrate was synthesized, and contrary to the reported difluoraminoacetate, the compound does not undergo dehydrofluorination on storage.

An NF-containing compound was obtained in the fluorination of 2,4,6-trichloroaniline. Instead of the originally expected 2,4,6-trichlorophenyldifluoramine, the compound appears to be a mixture of two fluoriminocyclohexadiene derivatives.

Synthesis, purification, and handling techniques in the preparation of fluoroammonium perchlorate were finalized and the compound now can be routinely prepared in lots of 2 to 3 grams.

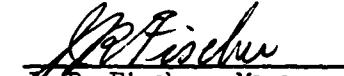
**CONFIDENTIAL**

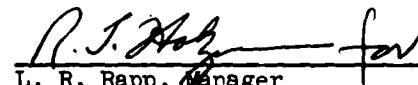
Report No. 0235-01-22

CONTRACT FULFILLMENT STATEMENT

This is the twenty-second in a series of quarterly technical reports submitted in partial fulfillment of the contract. It covers the period 1 January through 31 March 1965.

AEROJET-GENERAL CORPORATION

  
J. R. Fischer, Manager  
Chemical Department

  
L. R. Rapp, Manager  
Chemical and Structural Products Division

Page iii

**CONFIDENTIAL**

**CONFIDENTIAL**

Report No. 0235-01-22

**CONTENTS**

	<u>Page</u>
I. INTRODUCTION	1
II. TECHNICAL DISCUSSION	1
A. Reactions of Difluoramine	1
B. Direct Fluorination	7
C. Fluorammonium Salts	14
III. PERSONNEL	16
Table	
X-ray Diffraction Pattern of Fluoroammonium Perchlorate	1
Solubility of Fluoroammonium Perchlorate	2
Figure	
Proton NMR Spectrum of 1-Difluoraminobutane Rearrangement Product	1
Fluorine NMR Spectrum of 1-Difluoraminobutane Rearrangement Product	2
Fluorine NMR Spectrum of 2-Difluoraminobutane Rearrangement Product	3
Proton NMR Spectrum of 2-Difluoraminobutane Rearrangement Product	4
Proton NMR Spectrum of 2-Difluoraminobutane Rearrangement Product (2.5 to 3.1 ppm)	5
Infrared Spectrum of $\alpha$ -Bromo- $\alpha$ -fluoriminotoluene	6
Proton NMR Spectrum of $\alpha$ -Bromo- $\alpha$ -fluoriminotoluene	7
Fluorine NMR Spectrum of $\alpha$ -Bromo- $\alpha$ -fluoriminotoluene	8
Infrared Spectrum of N,N'-Dimethoxy-N,N'-dicarbethoxyhydrazine	9
Infrared Spectrum of Methyl $\alpha$ -Difluoraminobutyrate	10
Proton NMR Spectrum of Methyl $\alpha$ -Difluoraminobutyrate	11
Fluorine NMR Spectrum of Methyl $\alpha$ -Difluoraminobutyrate	12

**CONFIDENTIAL**

Report No. 0235-01-22

CONTENTS (cont.)

Figure

Infrared Spectrum of Methyl $\alpha$ -(N-carbomethoxy-N-fluoro)aminobutyrate	13
Proton NMR Spectrum of Methyl $\alpha$ -(N-carbomethoxy-N-fluoro)amino- butyrate	14
Fluorine NMR Spectrum of Methyl $\alpha$ -(N-carbomethoxy-N-fluoro)amino- butyrate	15
Proton NMR Spectrum of 2,4,6-Trichloroaniline Fluorination Product	16
Infrared Spectrum of 2,4,6-Trichloroaniline Fluorination Product	17
Infrared Spectrum of Fluoroammonium Perchlorate	18

**CONFIDENTIAL**

Report No. 0235-01-22

I. INTRODUCTION

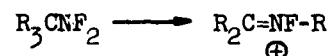
The objective of this program is to develop new methods of preparing high-energy materials for military application. During the period covered in this report, research has continued on the reactions of difluoramine, on liquid phase fluorination of nitrogenous compounds, and the preparation of fluoroammonium perchlorate.

II. TECHNICAL DISCUSSION

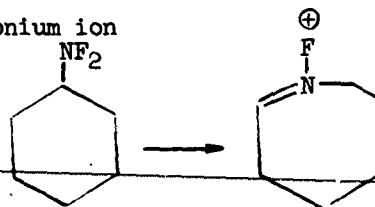
A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

The reactions of t-alkyldifluoramines with boron trifluoride or sulfuric acid have yielded N-fluoroimmonium ions by the loss of fluoride, with concomitant alkyl migration.\*



The only primary and secondary alkyl difluoramines that were examined in this reaction (using sulfuric acid) were ethyldifluoramine and cyclohexyldifluoramine. The former compound underwent eliminations of HF to form acetonitrile rather than rearrangement to an imonium ion. The latter compound rearranged as expected to give the cyclic imonium ion



\*Aerojet Report No. 2945, October 1964, p. 9 (Confidential).

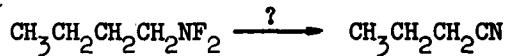
**CONFIDENTIAL**

## II Technical Discussion, A (cont.)

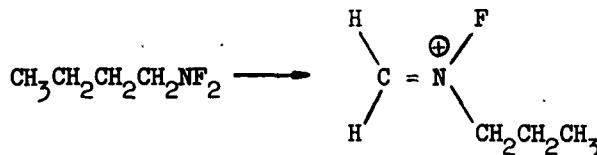
Report No. 0235-01-22

The potential usefulness of this reaction for predicting side-products in difluoramine reactions prompted the investigation of addition primary and secondary derivatives. The syntheses of 1-difluoraminobutane and 2-difluoraminobutane by the fluorination of n-butylurea and N-(2-butyl)carbamate, respectively, were given in the preceding report.\*

The reaction of 1-difluoraminobutane with sulfuric acid was expected to proceed in a way analogous to that of ethyldifluoramine, to give the nitrile



However, the NMR spectra of the solution formed by shaking 1-difluoraminobutane with sulfuric acid were consistent with the propyl migration product, N-fluoro-N-propyl-methyleneimonium ion



The proton NMR spectrum of the sulfuric acid solution is shown in Figure 1. The low-field group of signals is assignable to the "olefinic" protons. The inner two members are seen to be doublets, while the outer ones are broadened. It seems reasonable to assign the outer signals (8.41 ppm,  $j = 48$  cps) to the proton trans to fluorine and the inner ones (8.38 ppm,  $j = 23$  cps) to the cis proton. The splitting of the cis proton is attributed to geminal coupling to the trans proton. The trans proton signal would be broadened by allylic coupling to the  $\alpha$ -methylene proton of the propyl group. The pair of triplets at 4.46 ppm is assignable to these  $\alpha$ -methylene protons; the sextet at 2.10 ppm, to the next methylene, and the triplet at 1.12 ppm, to the methyl group.

\*Aerojet Report No. 0235-01-21, February 1965, p. 7 (Confidential).

**CONFIDENTIAL**

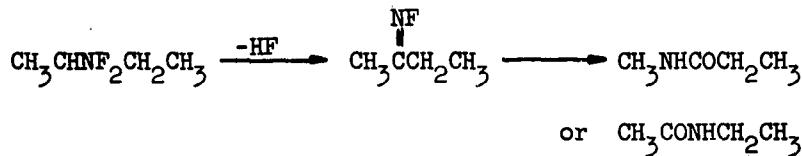
**CONFIDENTIAL**

## II Technical Discussion, A (cont.)

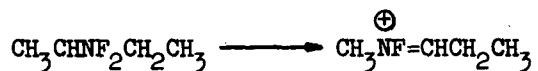
Report No. 0235-01-22

The  $F^{19}$  spectrum is given in Figure 2; an HF signal was observed at -116.55 ppm but is not shown in the figure. On the basis of the assignments of the "olefinic" protons, the NF signal would be expected to be a doublet (48 cps) of doublets (23 cps) of triplets (14 cps), as shown in the line spectrum. The predicted separation of the inner four members of the multiplet are 23, 25, and 23 cps; the observed separations are 21, 25, and 21 cps.

The reaction of 2-difluoraminobutane with sulfuric acid could be envisioned as taking place by any of three possible routes. Elimination of HF would give 2-fluoriminobutane, which would undergo a Beckmann rearrangement



Methyl migration would give N-fluoro-N-methylpropylidenimonium ion:



Ethyl migration, on the other hand, would give N-fluoro-N-ethylideneimonium ion:



When 2-difluoraminobutane was shaken with concentrated sulfuric acid at  $0^{\circ}\text{C}$ , a homogeneous solution was formed. The proton and fluorine NMR spectra of this solution showed that the latter course was followed. Thus, the  $F^{19}$  spectrum (Figure 3) consists of an overlapping pair of triplets at -122.67 ppm and a singlet at -116.79, assignable to HF. The proton spectrum (Figure 4) contains a pair of quartets at 4.44 ppm and a triplet at 1.65 ppm which are attributable to the ethyl group. A pair of quartets at 8.54 ppm is in agreement with the signal expected for the "olefinic" proton of the ethylidene group. The methyl signal appears as a pair of doublets at 2.67 and 2.61 ppm.

Peaks marked with an asterik are not assignable on the basis of the proposed structure, and are due to side-products or decomposition products.

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, A (cont.)

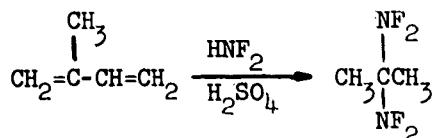
Report No. 0235-01-22

Acetaldehyde, the expected hydrolysis product, was found to be unstable under the reaction conditions, condensing to give crotonaldehyde in a very short time. Crotonaldehyde showed peaks at 2.50 and 2.63 ppm. Recording only the 2.5- to 3.1-ppm portion of the spectrum immediately after a fresh sample was prepared gave the curve showing the absence of these impurities (Figure 5).

The presence of two doublets for this methyl group is indicative of the presence of cis and trans formed (i.e., rotation about the imonium double bond is slower than is observable by NMR at this coupling constant). On the other hand, the absence of separate signals for the cis and trans configurations of the "vinyl" hydrogen and the observed 37-cps HF coupling constant, close to the average of the cis and trans signals for the 1-difluoraminobutane product, indicate averaging. The expected chemical shifts of the cis and trans protons should differ by about 0.03 ppm, by analogy to the observed shifts of the 1-difluoraminobutane product. Apparently the rate of rotation about the C-N bond is such as to average the smaller difference but not the larger one.

These results indicate a much higher migratory aptitude for higher alkyl groups than for methyl groups in this reaction. For the 2-difluoraminobutane product, a minor portion of the proton spectrum consists of peaks not assignable to the ethyl migration product. The fluorine spectrum does not indicate other products, although the resolution is limited. The reaction of 1-difluoraminobutane with sulfuric acid consisted almost entirely of rearrangement with propyl migration, although ethyldifluoramine underwent only elimination.

The reaction of isoprene with difluoramine in sulfuric acid has yielded 2,2-bis(difluoramino)propane.\*



This reaction, of possible utility for preparing high-energy propellant ingredients, may involve an alkylidifluoramine rearrangement similar to those above. The

\*Aerojet Report No. 2099, November 1961, p. 11 (Confidential).

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, A (cont.)

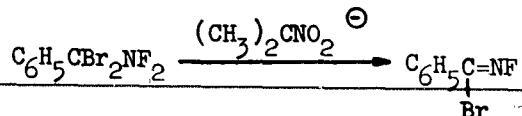
Report No. 0235-01-22

reaction was therefore repeated under conditions which do not normally result in rearrangement, using  $\text{BF}_3 \cdot \text{H}_2\text{PO}_4$  as the catalyst. The product was a 1:1 adduct, as shown by elemental analysis, but NMR analysis to determine the direction of addition has not yet been performed. The reaction of the adduct with sulfuric acid will be studied.

Although gem-difluoramines are stable in sulfuric acid under the preparative conditions, the possibility of reaction with sulfuric acid in the absence of difluoramine was examined. When a mixture of 2,2-bis(difluoramino)-octane and concentrated sulfuric acid was agitated vigorously at room temperature for 1 hour, a homogeneous solution was formed. The  $\text{F}^{19}$  NMR spectrum of this solution showed that HF was the only fluorine species present. The solution was quenched with ice and extracted with methylene chloride. The infrared spectrum of the methylene chloride solution showed only 2-octanone. The reaction of ketones with difluoramine is thus readily reversible.

The reactions of  $\alpha,\alpha$ -dibromo- $\alpha$ -difluoraminotoluene,  $\alpha$ -bromo- $\alpha,\alpha$ -bis(difluoramino)toluene and  $\alpha$ -difluoramino- $\alpha,\alpha$ -dichlorotoluene with sodium methoxide gave dimethyl carbonate anil.\* Some reactions of these NF compounds with other basic reagents were also explored. Reactions with tertiary amines gave only tars. Secondary amines gave products which appeared, on the basis of infrared spectra, to be the tetraalkylguanidines corresponding to the above reactions, but elemental analyses were unsatisfactory.

The sodium 2-propanenitronate in methanol reacted with  $\alpha,\alpha$ -dibromo- $\alpha$ -difluoraminotoluene to give  $\alpha$ -bromo- $\alpha$ -fluoriminotoluene. Although an uncontaminated sample could not be obtained by gas chromatography; elemental analysis was in fair agreement with the theoretical values; and the structure was confirmed by infrared (Figure 6), proton (Figure 7), and fluorine (Figure 8) NMR spectra.



\* Aerojet Report No. 0235-01-21, February 1965, p. 3 (Confidential).

**CONFIDENTIAL**

**CONFIDENTIAL**

A reduction of this type is probably the first step in the methoxide reaction leading to dimethyl carbonate anil. In the nitronate reaction, subsequent addition to the fluorimino could be inhibited because of the size of the anion.

2. Experimental

a. Reaction of Alkyldifluoramines with Sulfuric Acid

The alkyldifluoramine (0.05 ml) was added to 1 ml of sulfuric acid at 0°C in a stoppered test tube. The tube was agitated with a vortex mixer, with intermittent cooling with an ice bath, until a homogeneous solution was formed. NMR spectra of these solutions were obtained.

b. Reaction of Isoprene with Difluoramine

Boron trifluoride complex of phosphoric acid (1 ml) was added with stirring to a refluxing mixture of 5 g of isoprene and 27 g of difluoramine. After 2.5 hours, 50 ml of pentane was added and the excess difluoramine was vented off. Distillation of the pentane solutions gave 0.35 g of liquid, bp 52°C/0.15 mm.

Anal. Calc'd for  $C_5H_9NF_2$ : C, 49.5; H, 7.34; N, 11.55; F, 31.40.

Found: C, 48.5; H, 7.12; N, 12.1; F, 29.9.

c. Reaction of Dibromodifluoraminotoluene with Sodium 2-Propane-Nitronate

A solution of sodium 2-propanenitronate was prepared by refluxing a mixture of 11.1 ml (0.0163 moles) of 1.47 M methanolic sodium methoxide and 1.45 g (0.0163 moles) of 2-nitropropane for 30 min. This solution was cooled to room temperature and 2.45 g (0.00815 moles) of dibromodifluoraminotoluene in 35 ml of methanol was added over a 15 min period. After 1 hour, the methanol was removed under vacuum and hexane was added. The hexane solution was filtered and distilled to give 0.98 g of liquid, bp 52°C/0.75 mm.

Gas chromatography (1/4-in. by 12 ft column of 10% SE-30 silicone on Teflon, 110°C) showed a major component comprising 85% of the sample

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, A (cont.)

Report No. 0235-01-22

and six volatile contaminants. Characterization of the major component indicated that it was  $\alpha$ -bromo- $\alpha$ -fluoriminotoluene, with some impurities.

Anal. Calc'd for  $C_7H_5NFBr$ : C, 41.6; H, 2.48; N, 6.94; F, 9.4.

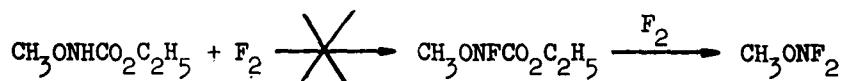
Found: C, 42.0; H, 2.64; N, 8.47; F, 10.1.

The infrared spectrum is shown in Figure 6. The proton and fluorine NMR spectra (Figures 7 and 8, respectively) were obtained using a Varian microcell, with  $CDCl_3$  as solvent and  $CFCl_3$  and TMS as internal references. The proton spectrum consists of a complex aromatic multiplet with prominent absorptions at 448 and 463 cps, a doublet at 4.09 ppm, and a singlet at 1.68 ppm (caused by impurities). The fluorine spectrum consists of a somewhat broadened fluorimino band at -64.1 ppm.

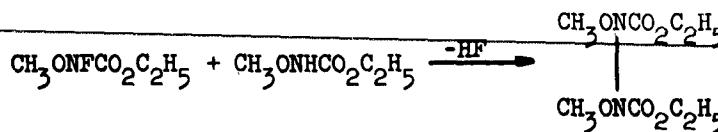
**B. DIRECT FLUORINATION (V. Grekauskas)****1. Discussion**

The study of liquid-phase fluorination of nitrogenous organic compounds was continued using acetonitrile as the solvent.

The fluorination of ethyl methoxycarbamate in acetonitrile was investigated with the objective of synthesizing either its N-fluoro derivative or O-methyl-N,N-difluorohydroxylamine:



Neither compound was obtained; instead the reaction product was identified as  $N,N'$ -dimethoxy- $N,N'$ -dicarbethoxyhydrazine on the basis of its elemental analysis, and its infrared (Figure 9) and proton NMR Spectra. The compound apparently was formed in a coupling reaction between N-fluoro-N-methoxycarbamate and methoxycarbamate:

**CONFIDENTIAL**

**CONFIDENTIAL**

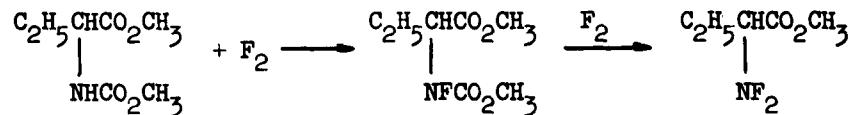
II Technical Discussion, B (cont.)

Report No. 0235-01-22

*N,N'*-Dimethoxy-*N,N'*-dicarbethoxyhydrazine represents the first known *N*-alkoxy-substituted hydrazine derivative. One unsuccessful attempt was made to hydrolyze the compound to *N,N'*-dimethoxyhydrazine; it reacted readily with cold concentrated hydrochloric acid with the evolution of carbon dioxide, but only a trace amount of an unidentified solid was isolated from the reaction mixture.

*N,N'*-Dimethoxy-*N,N'*-dicarbethoxyhydrazine appears to be an interesting substrate for studying its fluorination and in order to obtain larger amounts of the compound one attempt was made to "couple" ethyl methoxycarbamate with bromine in carbon tetrachloride solution; however, reaction did not take place at ambient temperature.

Ethyl difluoraminoacetate was previously obtained in the fluorination of ethyl *N*-carbomethoxyglycine.\* The compound, however, could not be separated completely from its dehydrofluorination product, ethyl cyanoformate. It appeared that the instability of  $\alpha$ -difluoraminocarboxylic acid esters might be characteristic only to the first member of the series, and now has been found to be the case. Methyl  $\alpha$ -difluoraminobutyrate, synthesized in the fluorination of methyl  $\alpha$ -carbomethoxyaminobutyrate in acetonitrile solution, was found to be stable and storable at room temperature.



The compound was characterized on the basis of its elemental analysis, and its infrared (Figure 10) and NMR (Figures 11 and 12) spectra.

Methyl  $\alpha$ -(*N*-carbomethoxy-*N*-fluoro)aminobutyrate was also obtained in the above fluorination and the compound was fully characterized by its infrared and NMR spectra (Figures 13, 14, and 15).

The fluorination of aromatic nitrogenous compounds was attempted on several occasions in the past, but the reaction produced large amounts of tar

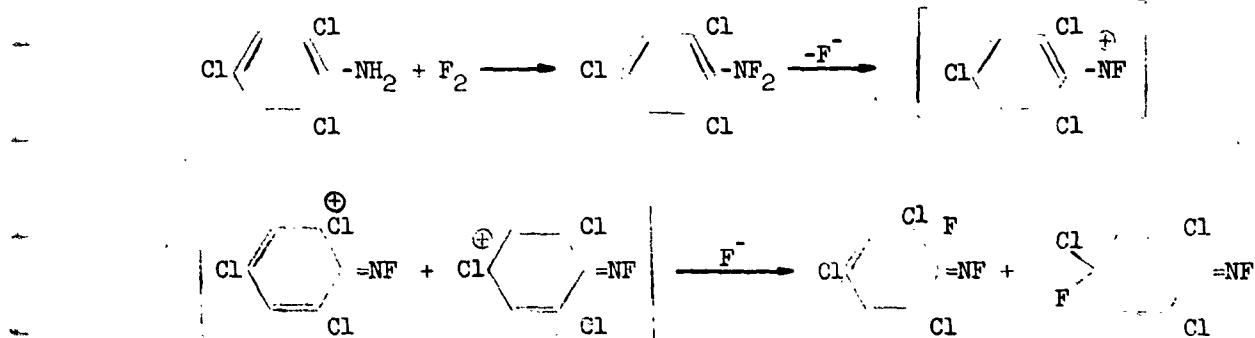
\*Aerojet Report No. 2730 (Annual Summary), October 1963, p. 25 (Confidential).

**CONFIDENTIAL**

II Technical Discussion, B (cont.)

Report No. 0235-01-22

and isolation and characterization of reaction products was found impossible. From these unsuccessful attempts, it was learned that the fluorination of negatively substituted aromatic compounds proceeds "cleaner." However, the solubility of such substrates in water is extremely low and the fluorination under such conditions is impractical. The finding that acetonitrile is a very suitable solvent for liquid phase fluorination, in conjunction with the increased solubility of organic compounds in this solvent, suggested that the fluorination of aromatic nitrogenous compounds might proceed better under these conditions than in aqueous suspensions. On the basis of these considerations, the fluorination of 2,4,6-trichloroaniline was investigated. The fluorination still was sluggish and the reaction mixture turned gradually black during the course of the reaction. However, on working up the product by fractional distillation, a small amount (ca. 5% yield) of liquid was obtained and its elemental analysis compared well with that calculated for 2,4,6-trichlorophenyldifluoramine. Its proton NMR spectrum (Figure 16), however, indicated that the compound was not the desired difluoramine derivative, but most likely a mixture of two trichlorocyclohexadienefluorimino isomers. The reaction can be rationalized by the formation of the difluoramine, followed by its rearrangement:



The infrared spectrum of the material is shown in Figure 17. The rearrangement might have taken place spontaneously during the process of fluorination. On the other hand, it is also possible that it was effected during the fractionation of the crude reaction product when the mixture was kept at 70 to 90°C for a period of several hours.

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, B (cont.)

Report No. 0235-01-22

2. Experimental

a. Fluorination of Ethyl Methoxycarbamate

A solution of 18 g (0.15 mole) of ethyl N-methoxycarbamate in 120 ml of acetonitrile was fluorinated at -15 to -25°C until 3.5 liters of fluorine (~0.15 mole) was consumed. The fluorination mixture was added to 550 ml of ice water and insoluble material was separated and worked up to give 3 g of a pale-yellow oil, bp 90 to 91°C/0.1 mm, which was identified as N,N'-dimethoxy-N,N'-dicarbethoxyhydrazine.

Anal. Calc'd for  $C_8H_{16}N_2O_6$ : C, 40.68; H, 6.83; N, 11.86.

Found: C, 40.3; H, 6.4; N, 11.9.

DTA of this compound showed a strong exotherm at 142°C. Its infrared spectrum is shown in Figure 9. The 60-mc proton NMR spectrum was obtained, using a  $CDCl_3$  solution with TMS added as an internal reference. The assignments are as follows: the triplet at 1.33 ppm and the quartet at 4.31 ppm are assigned to the ethyl group; the intense singlet at 3.87 ppm is assigned to the methoxy methyl group.

b. Fluorination of Methyl  $\alpha$ -Carbomethoxyaminobutyrate

Methyl  $\alpha$ -carbomethoxyaminobutyrate was synthesized by reacting DL- $\alpha$ -aminobutyric acid with methyl chloroformate in aqueous sodium hydroxide solution to give  $\alpha$ -carbomethoxyaminobutyric acid which was then esterified with methanol. The material, bp 75 to 6°C/0.1 mm, was obtained in 85% yield.

Anal. Calc'd for  $C_7H_{13}NO_9$ : C, 48.0; H, 7.5; N, 8.0.

Found: C, 47.8; H, 7.8; N, 8.4.

A solution of 70 g (0.4 mole) of methyl  $\alpha$ -carbomethoxyaminobutyrate in 300 ml of acetonitrile was fluorinated at 0 to 5°C until ca. 0.7 moles of fluorine was consumed. The fluorination mixture was washed with 600 ml of ice water, phases separated, and the product was washed with three 150-ml portions of ice water. The crude material, 65 g, was dried and worked up to give

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, B (cont.)

Report No. 0235-01-22

22 g of methyl  $\alpha$ -difluoraminobutyrate, bp 52 to 3°C/40 mm, and 34 g of methyl  $\alpha$ -(N-carbomethoxy-N-fluoramino)butyrate, bp 48 to 9°C/0.3 mm.

The infrared spectrum of methyl  $\alpha$ -difluoraminobutyrate is shown in Figure 10.

Anal. Calc'd for  $C_5H_9NF_2O_2$ : C, 39.2; H, 5.92; N, 9.15; F, 24.81.

Found: C, 39.5; H, 6.1; N, 9.5; F, 23.4.

The 60-mc proton (Figure 11) and 56.4-mc fluorine (Figure 12) NMR spectra were obtained using  $CDCl_3$  solution with TMS and  $CFCl_3$  added as internal references. The assignments are as follows:

H'. The triplet at 1.03 ppm is assigned to the  $CH_3CH_2-$  methyl group. The slightly irregular quartet at 1.95 ppm is assigned to the  $CH_3CH_2CH-$  methylene. The asymmetry of the carbon to which it is attached appears to have little effect on the signal. The intense singlet at 3.81 ppm is assigned to the carbomethoxy methyl group. The doublet of doublets (coupling constants of  $25.7 \pm 0.7$  cps and  $24.4 \pm 0.8$  cps, coupling to nonequivalent  $NF_2$  fluorines) of triplets (coupling to adjacent  $-CH_2-$ ) at 4.10 ppm is assigned to the  $-CH_2CHNF_2-$  proton.

F<sup>19</sup>. The fluorine spectrum consists of an AB quartet (chemical shifts -43.10 and -50.66 ppm, coupling constant  $592.4 \pm 0.4$  cps). The fluorines are rendered nonequivalent by the virtue of the attachment of the  $-NF_2$  group to an asymmetric carbon. The quartet components are further split into doublets ( $25.5 \pm 0.8$  cps,  $24.0 \pm 0.8$  cps) by coupling to the proton on that carbon. The observed coupling constants are in good agreement with those obtained from the proton spectrum. The proton and fluorine NMR spectra are consistent with each other and with the methyl  $\alpha$ -difluoraminobutyrate structure.

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, B (cont.)

Report No. 0235-01-22

The infrared spectrum of methyl  $\alpha$ -(N-fluoro-N-carbo-methoxy)aminobutyrate is shown in Figure 13.

Anal. Calc'd for  $C_7H_{12}NFO_4$ : C, 43.5; H, 6.3; N, 7.3; F, 9.8.

Found: C, 43.5; H, 6.2; N, 7.4; F, 10.5.

The 60-mc proton (Figure 14) and 56.4-mc fluorine (Figure 15) NMR spectra were obtained in  $CDCl_3$  solution, with TMS and  $ClCl_3$  added as internal references. The assignments are as follows:

H'. The triplet at 1.10 ppm is assigned to the  $CH_3CH_2$ - methyl group. The multiplet with the maximum intensity at 124 cps is assigned to the  $CH_3CH_2CH$ - methylene. The complex nature of this signal is attributable to the asymmetry of the carbon to which the methylene is attached and probably also to a small coupling to the -NF- fluorine. The intense singlets at 3.79 and 3.92 ppm are assigned to the carbomethoxy methyls. Each appears to be accompanied by a weaker signal to high field. This may be a consequence of partial double bond character of the -N-C- bond with resultant cis-trans isomerism. The doublet ( $40.5 \pm 0.6$  cps, coupling to NF fluorine) of doublets of doublets (different couplings to the  $-CH_2$ - protons) at 4.59 ppm is assigned to the  $-CH_2CHNF$ - proton.

F<sup>19</sup>. The fluorine spectrum consists of a strong doublet ( $40.8 \pm 0.5$  cps) at +81.43 ppm and a weaker doublet ( $11.2 \pm 0.5$  cps) at +79.98 ppm. The splitting in the stronger doublet is in excellent agreement with that observed in the proton spectrum and the signal is assignable to the -NFCO- fluorine. The weaker doublet may then be assigned to the corresponding cis or trans isomer. In this case, however, the large difference in the splittings is difficult to explain.

c. Fluorination of 2,4,6-Trichloroaniline

A solution of 19.6 g (0.1 mole) of 2,4,6-trichloroaniline in 200 ml of acetonitrile was fluorinated at 0°C until 4.5 liters of fluorine was

**CONFIDENTIAL**

**CONFIDENTIAL**

II Technical Discussion, B (cont.)

Report No. 0235-01-22

consumed. The fluorination mixture was added to 700 ml of ice water and phases were separated. The dark, viscous organic product was washed with water and dissolved in 75 ml of methylene chloride. The dried solution was worked up to give 2.0 g of orange-yellow liquid, bp 45 to 50°C/0.2 mm. The elemental analysis of the product was in excellent agreement with that calculated for 2,4,6-trichlorophenyldifluoramine.

Anal. Calc'd for  $C_6H_2NF_2Cl_3$ : C, 31.0; H, 0.9; N, 6.0; F, 16.4.

Found: C, 31.2; H, 1.1; N, 5.2; F, 16.4.

The infrared spectrum of the material is shown in Figure 17.

The 60-mc proton NMR spectrum (Figure 16) was obtained using  $CDCl_3$  solution, with TMS added as internal reference. The spectrum is quite complex, consisting of a multiplet (or group of multiplets) at low field, with prominent lines at 394, 409, 430, and 436 cps and a much weaker group of signals to high field (most intense line at 137 cps). Other weak, broad signals are also apparent. The low-field signals are in the region usually characteristic of aromatic protons. However, olefinic protons also may appear in this vicinity.

The spectrum is much too complicated for the symmetrical difluoro-2,4,6-trichloroaniline. However, if the rotation of the difluor amino group is hindered by the ortho chlorines, the  $NF_2$  fluorines would be rendered non-equivalent which might complicate the proton spectrum considerably. The complexity could also result from the presence of a mixture of the two rearrangement products.

The fluorine NMR spectrum has been obtained only in a preliminary manner using  $CFCl_3$  as internal reference. The spectrum appears to consist of two groups of signals, one in the vicinity of -30 ppm and the other near +100 ppm. This information rules out the presence of the difluor amino derivatives alone, since it offers no explanation of the signals to the high field. These signals are in the region characteristic of CF fluorines, suggesting the presence of either one or both rearrangement products. The low-field signals are attributable to  $=NF$  or  $-NF_2$  fluorines or a combination of both.

**CONFIDENTIAL**

## CONFIDENTIAL

### II Technical Discussion (cont.)

Report No. 0235-01-22

#### C. FLUORAMMONIUM SALTS (A. Remanick, V. Grakauskas, and H. J. Marcus)

##### 1. Discussion

During this report period, several 2-3 g batches of N-fluorammonium perchlorate (SAP) were prepared for physical and chemical testing. The material was routinely purified by sublimation at 65°C/0.05 mm. Although sublimation sufficed as a purification technique for the 2- to 5-g quantities, anticipation of the need for larger amounts of SAP prompted the investigation of an alternate purification method. It was found the crude SAP could be purified by liquid-solid chromatography on silica gel using ethyl acetate as the eluent, followed by precipitation with chloroform. Elemental analysis and proton NMR spectrum showed that SAP purified in this manner did not contain foreign materials.

The infrared spectrum of SAP is given in Figure 18. The spectrum was obtained by subliming SAP onto a sodium chloride window. The N-F absorption is apparently obscured by the  $\text{ClO}_3$  absorption; both NH-stretch ( $3.05\mu$ ) and NH-bend ( $7.03\mu$ ) vibrations are shifted by approximately  $0.15\mu$  to shorter wavelength as compared with those of ammonium perchlorate.

The X-ray powder diffraction pattern is given in Table 1.

Some additional solubility data for SAP is given in Table 2.

The previously reported impact sensitivity of sublimed SAP was studied further. The material shows no firing below 20 cm (2 kg) and the 50% level varies between 25 and 30 cm (2 kg) (50% RDX = 25 cm). The determination of SAP's sensitivity to static electrical charge is now in progress.

The storage stability tests of SAP were continued. It was previously established that SAP decomposes slowly (over 4 to 7 days) in glass containers at room temperature but is stable for as long as 1 month at  $-20^{\circ}\text{C}$ . It has been found that in nickel or monel containers the material is stable for at least two months at room temperature. There is some attack of the metal surface, but the bulk of the SAP apparently remains unaffected. In Teflon containers SAP decomposes gradually within one month, but the test results have been somewhat erratic. In 320 stainless steel, there is a marked degree of decomposition within 1 month and much corrosion of the metallic surface.

## CONFIDENTIAL

## CONFIDENTIAL

### II Technical Discussion, C (cont.)

Report No. 0235-01-22

Thus, the work of the past several months on the synthesis of SAP can be summarized as follows: The compound can be now readily synthesized in 2- to 3-g batches and the material is storable at room temperature in nickel or monel containers in dry atmosphere for at least several months, and probably much longer. The compound is only moderately sensitive to impact and, in this respect, does not present any handling problems. The preliminary testing data indicates that SAP is not sensitive to static electrical charge and a more thorough study of this property is now in progress. If the results of this latter testing confirm our preliminary findings, SAP can be synthesized in much larger batches using only nominal safety precautions.

As pointed out on several occasions in earlier reports, SAP represents a unique NF compound certainly of theoretical and potentially of practical importance. The determination of its heat of formation, therefore, would be of utmost importance, and arrangements have been made with Mr. Fasolino of the National Research Corporation to study SAP on their Office of Naval Research program.

#### 2. Experimental

##### Purification of Fluorammonium Perchlorate

A column of 22-mm internal diameter provided with a Teflon stopcock was packed with a suspension of silica gel in ethyl acetate. The adsorbent (grade 12, 28 to 200 mesh) was activated by heating for 18 hours at 185°C. A solution of 1.85 g of crude SAP (containing 1.85% C) in 10 ml ethyl acetate was introduced into the column over a period of 37 minutes. The column was then washed with 55 ml of fresh solvent. Elution took place at the rate of about 1.7 ml/min. Most of the solvent was removed from the solution under reduced pressure, leaving a solution of 6- to 8-ml volume. Dilution with about 3 volumes of chloroform caused precipitation of the product which was separated by filtration, washed well with chloroform, and dried overnight under vacuum. The colorless product weighed 1.17 ;.

Anal. Found: C, 0.22.

## CONFIDENTIAL

**CONFIDENTIAL**

Report No. 0235-01-22

III. PERSONNEL

The experimental work was performed by K. Baum, V. Grakauskas, H. Marcus, M. P. Mascari, A. H. Remanick, and O. S. Schaeffler. Analytical support was provided by C. L. Deuel (gas chromatography), K. Inouye (microanalyses), and H. Nelson (IR and NMR).

**CONFIDENTIAL**

**CONFIDENTIAL**

Report No. 0235-01-22

TABLE 1

X-RAY DIFFRACTION PATTERN OF FLUOROAMMONIUM PERCHLORATE

<u><math>d^{\circ}A</math></u>	<u><math>I/I_0</math></u>	<u><math>d^{\circ}A</math></u>	<u><math>I/I_0</math></u>
9.60	w	3.11	s
8.26	vw	29.3	w
7.53	w	2.78	vw
6.70	vvw	2.63	w
6.23	vvw	2.53	w
5.26	m	2.45	2
4.82	wm	2.29	vw
4.09	w	2.18	vw
3.64	m	1.95	vw
3.43	m	1.82	w
3.29	w		

Table 1

**CONFIDENTIAL**

**CONFIDENTIAL**

Report No. 0235-01-22

TABLE 2

SOLUBILITY OF FLUOROAMMONIUM PERCHLORATE

Key: i, insoluble; d, soluble with decomposition; s, soluble

<u>Solvent</u>	<u>Behavior of Fluoroammonium Perchlorate</u>
Nitrobenzene	i
1,2-dichlorobenzene	i
Cyclohexane	i
Benzene	i
Chloroform	i
Carbon tetrachloride	i
Diisopropyl ether	d
Ethanol	d
Methanol	d
Ethyl acetate	s
Amyl acetate	s
Tetrahydrofuran	s
Monoglyme	s
Acetonitrile	s

Table 2

**CONFIDENTIAL**

CONFIDENTIAL

Report No. 0235-01-22

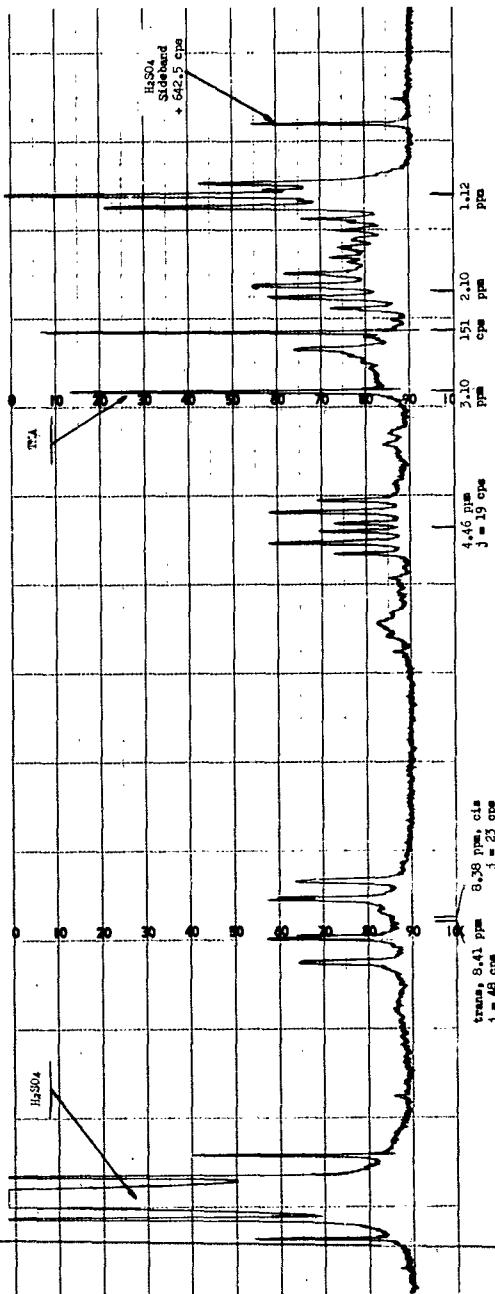


Fig. 1. Proton NMR Spectrum of 1-Difluoraminobutane Rearrangement Product

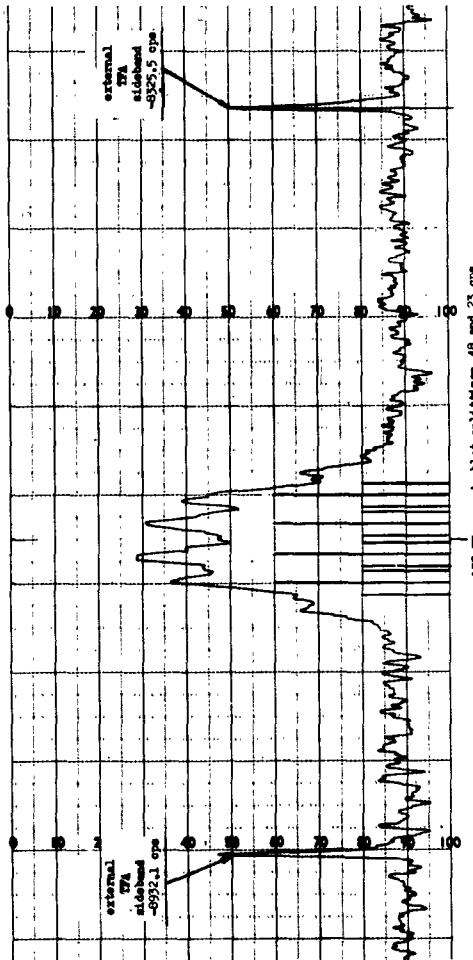


Fig. 2. Fluorine NMR Spectrum of 1-Difluoraminobutane Rearrangement Product

CONFIDENTIAL

Figures 1 and 2

**CONFIDENTIAL**

Report No. 0235-01-22

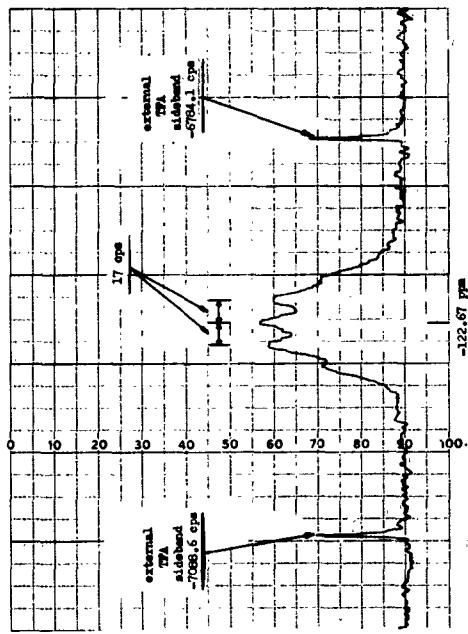


Fig. 3. Fluorine NMR Spectrum of 2-Difluoraminobutane Rearrangement Product

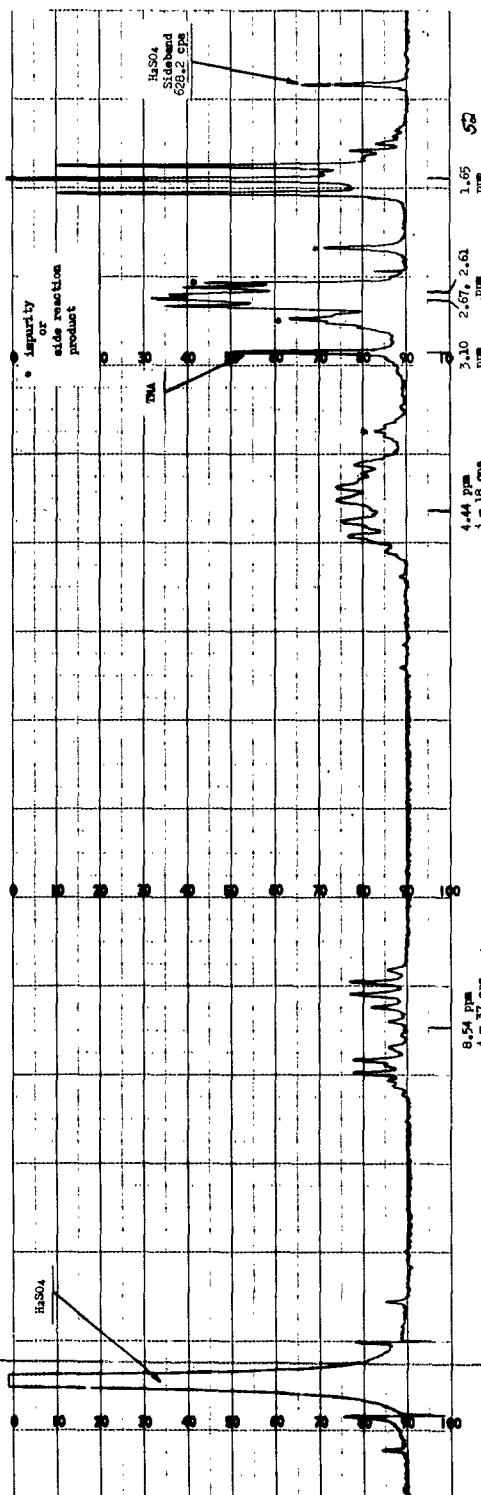


Fig. 4. Proton NMR Spectrum of 2-Difluoraminobutane Rearrangement Product

**CONFIDENTIAL**

Figures 3 and 4

**CONFIDENTIAL**

Report No. 0235-01-22

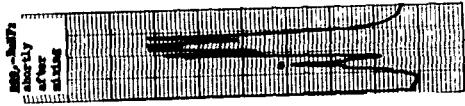


Fig. 5. Proton NMR Spectrum of 2-Difluoreminobutane  
Rearrangement Product (2.5 to 3.1 ppm)

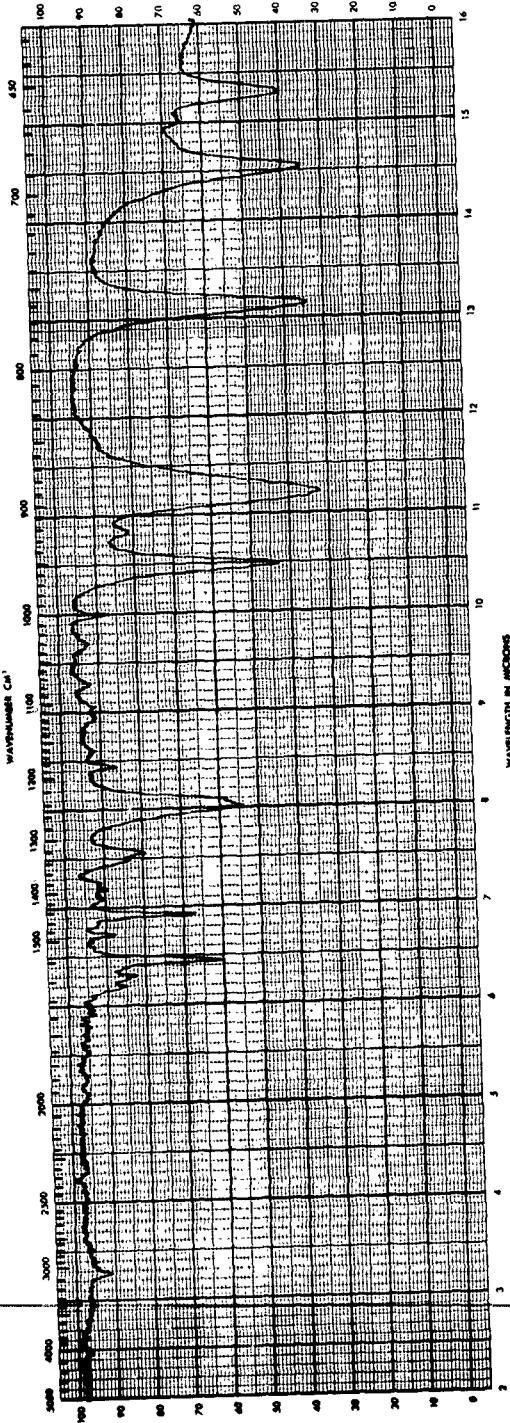


Fig. 6. Infrared Spectrum of  $\alpha$ -Bromo- $\alpha$ -fluoriminotoluene

**CONFIDENTIAL**

Figures 5 and 6

**CONFIDENTIAL**

Report No. 0235-01-22

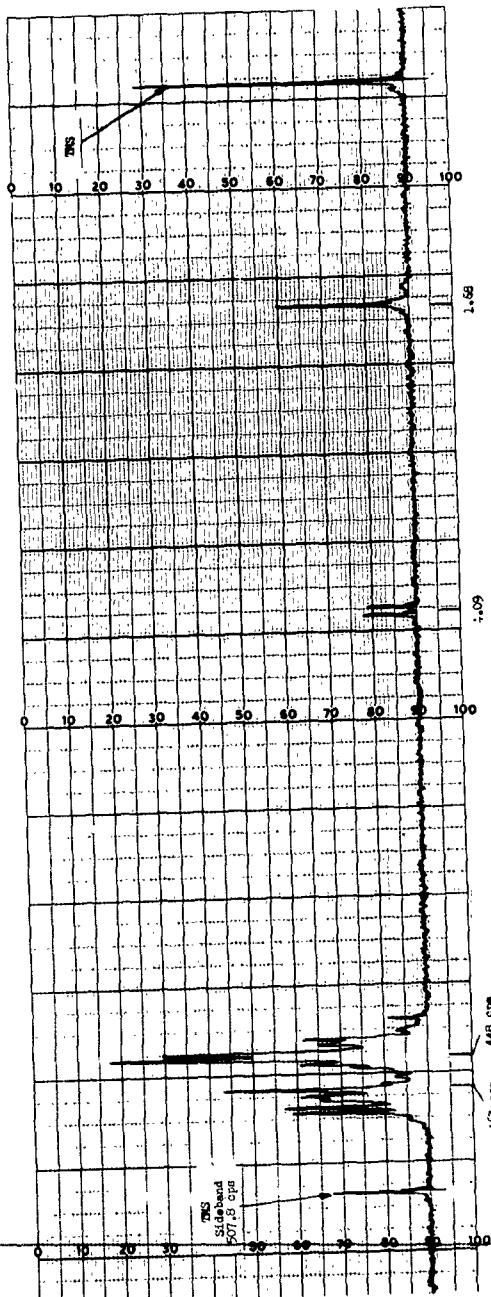


Fig. 7. Proton NMR Spectrum of  $\alpha$ -Bromo- $\alpha$ -fluoromethyltoluene

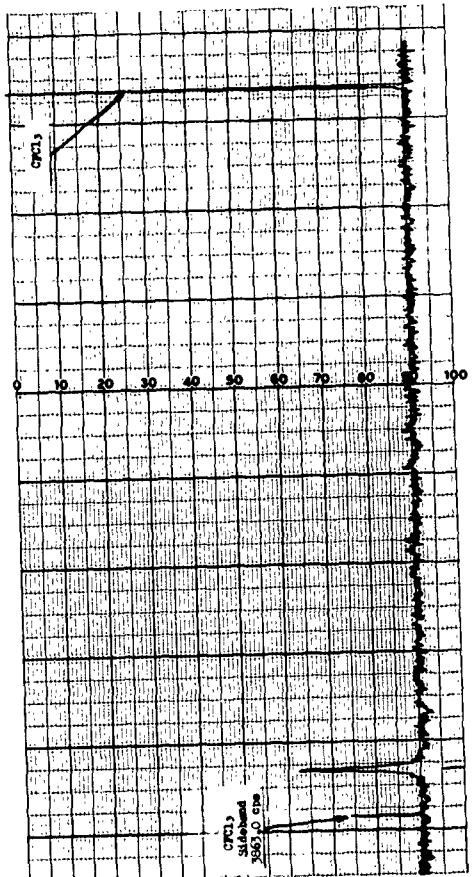


Fig. 8. Fluorine NMR Spectrum of  $\alpha$ -Bromo- $\alpha$ -fluoromethyltoluene

**CONFIDENTIAL**

Figures 7 and 8

**CONFIDENTIAL**

Report No. 0235-01-22

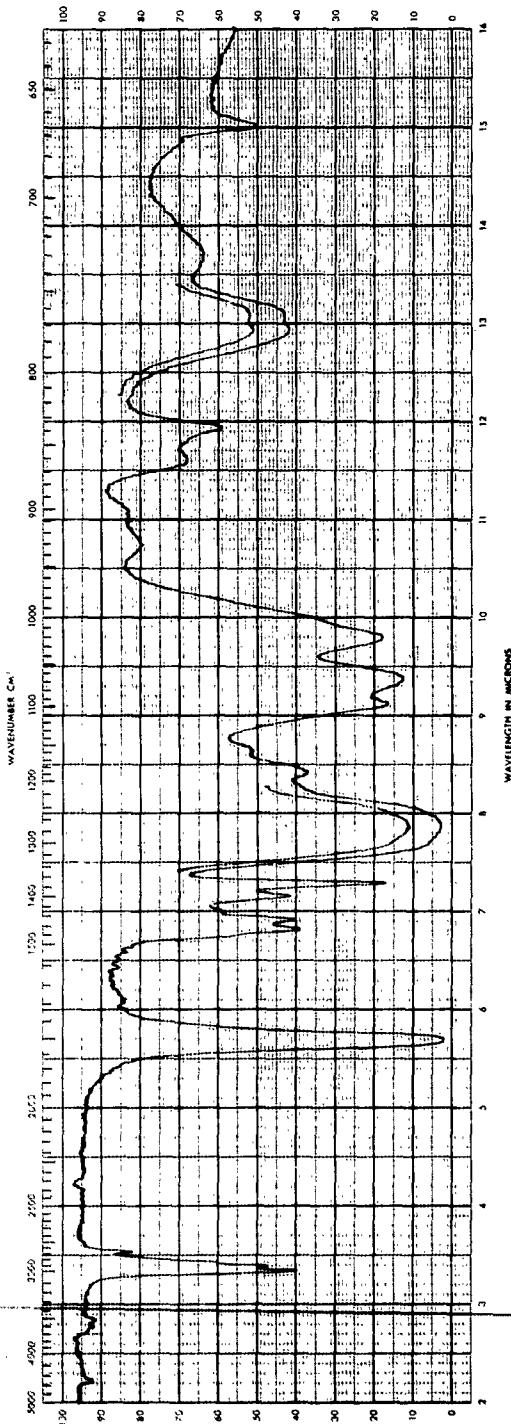


Fig. 9. Infrared Spectrum of  $N,N'$ -Dimethoxy- $N,N'$ -dicarbethoxyhydrazine

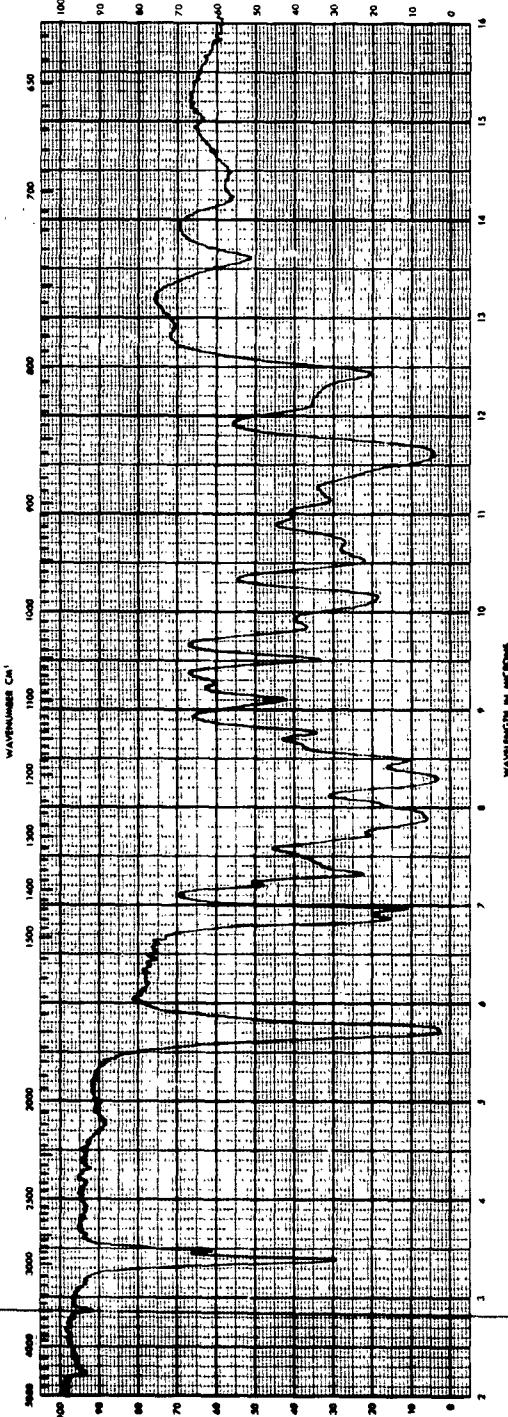


Fig. 10. Infrared Spectrum of Methyl  $\alpha$ -Difluoromethylbutyrate

**CONFIDENTIAL**

Figures 9 and 10

**CONFIDENTIAL**

Report No. 0235-01-22

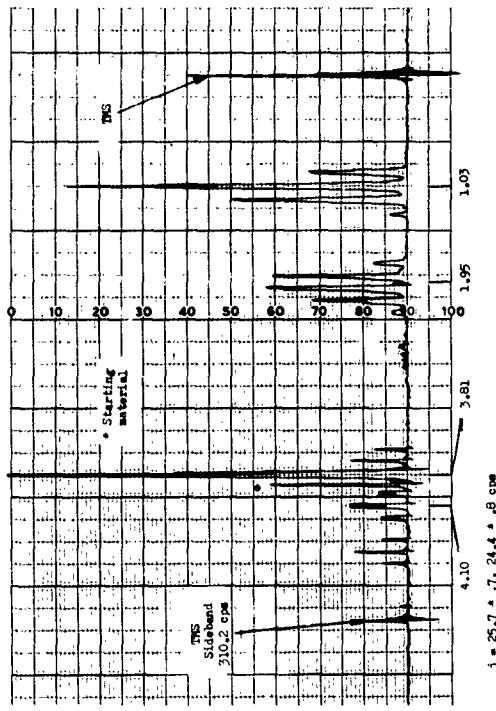


Fig. 11. Proton NMR Spectrum of Methyl  $\alpha$ -Difluororaminobutyrate

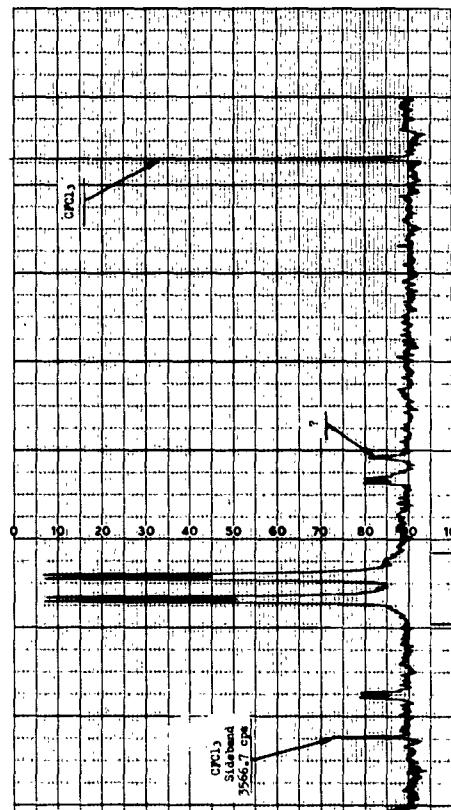


Fig. 12. Fluorine NMR Spectrum of Methyl  $\alpha$ -Difluororaminobutyrate

**CONFIDENTIAL**

Figures 11 and 12

**CONFIDENTIAL**

Report No. 0235-01-22

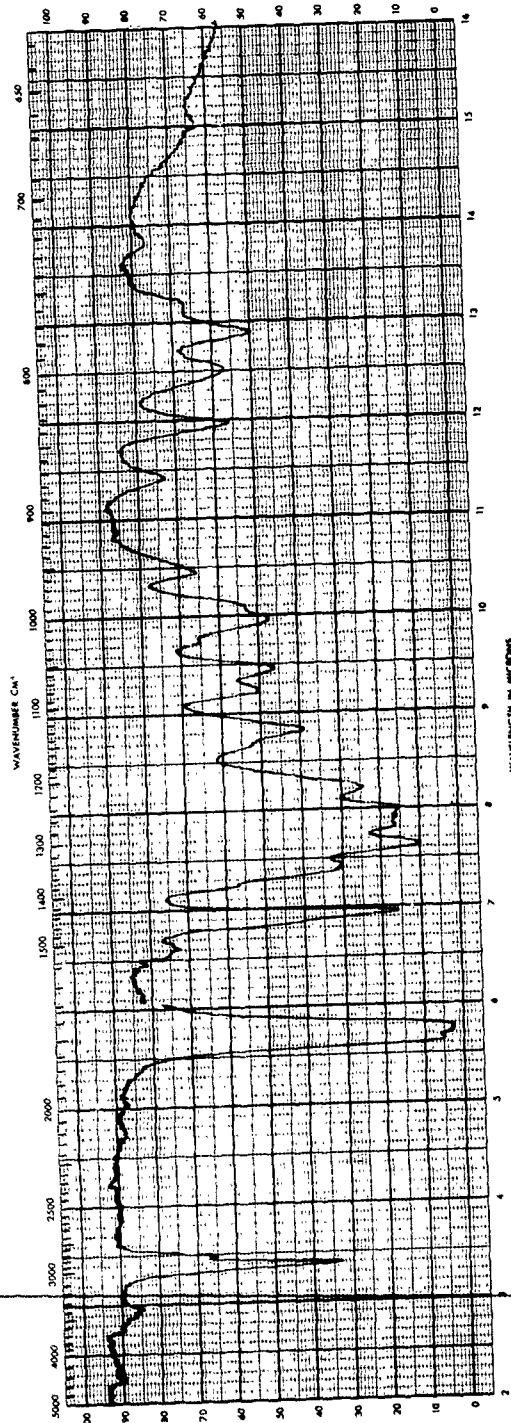


Fig. 13. Infrared Spectrum of Methyl  
 $\alpha$ -(N-carbomethoxy-N-fluoro)aminobutyrate

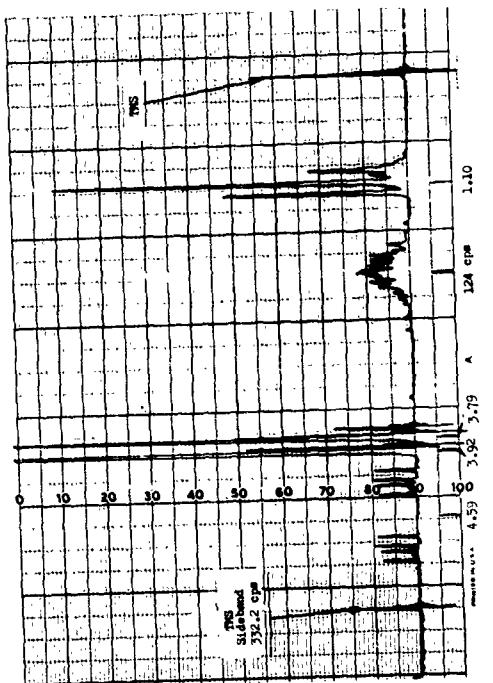


Fig. 14. Proton NMR Spectrum of Methyl  
 $\alpha$ -(N-carbomethoxy-N-fluoro)aminobutyrate

**CONFIDENTIAL**

Figures 13 and 14

**CONFIDENTIAL**

Report No. 0235-01-22

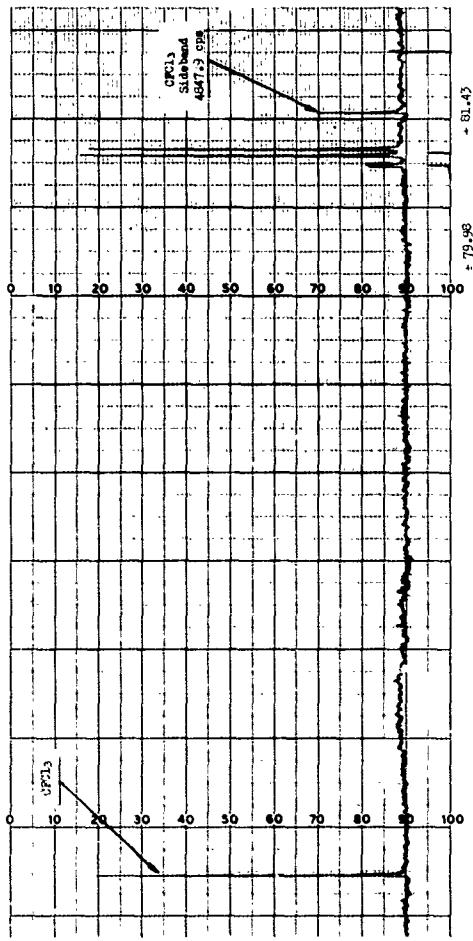


Fig. 15. Fluorine NMR Spectrum of Methyl  
 $\alpha$ -(N-carbomethoxy-N-fluoro)aminobutyrate

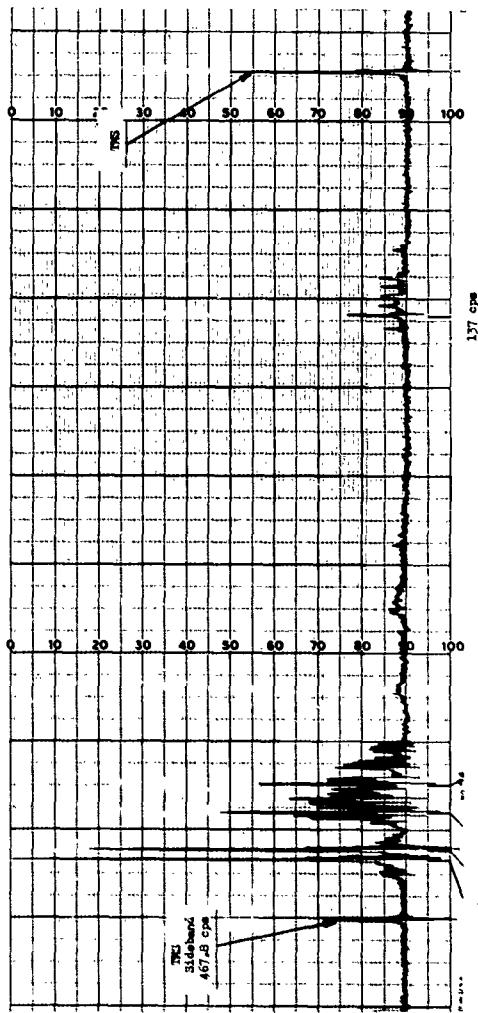


Fig. 16. Proton NMR Spectrum of 2,4,6-Trichloroaniline Fluorination Product

**CONFIDENTIAL**

Figures 15 and 16

**CONFIDENTIAL**

Report No. 0235-01-22

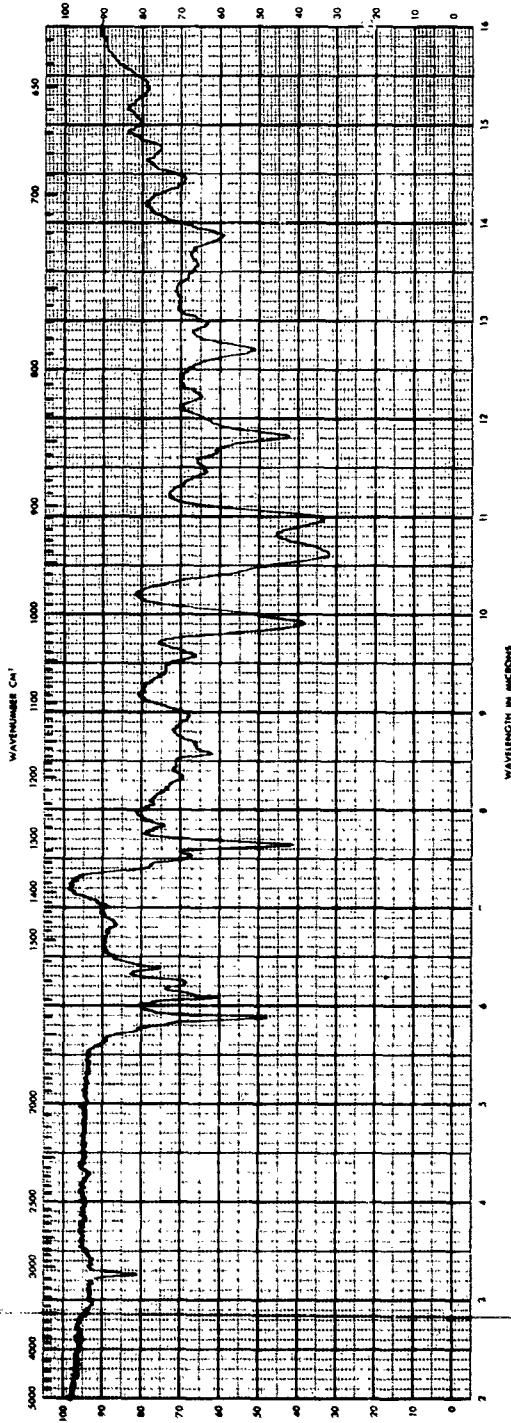


Fig. 17. Infrared Spectrum of 2,4,6-Trichloroaniline Fluorination Product

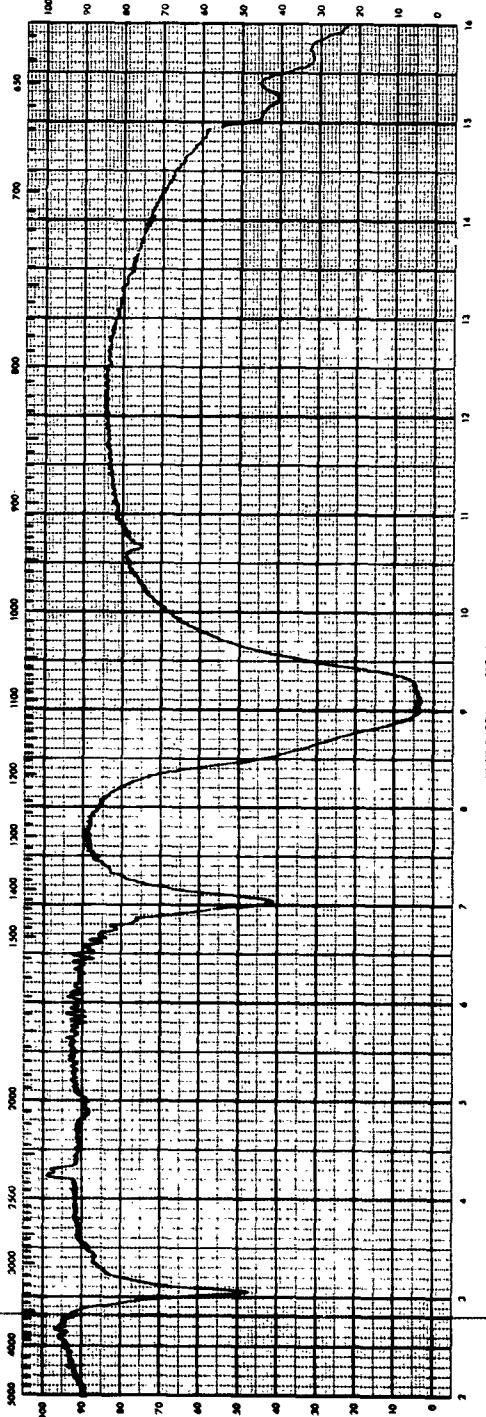


Fig. 18. Infrared Spectrum of Fluoroammonium Perchlorate

**CONFIDENTIAL**

Figures 17 and 18

**UNCLASSIFIED**

Report No. 0235-01-22

**DISTRIBUTION LIST**

**No. of Copies**

Chief, Office of Naval Research Department of the Navy Washington 25, D.C. Attn: Power Branch - Code 429	11
BuWepsRep., Azusa	1
Director Advanced Research Projects Agency The Pentagon Washington 25, D.C. Attn: Technical Information Officer	6
Dr. D. V. Sickman Naval Ordnance Laboratory White Oak, Silver Spring, Maryland	1
Commanding Officer Army Chemical Center, Maryland Attn: Technical Library	1
Los Alamos Scientific Laboratory Los Alamos, New Mexico Attn: Technical Library	2
Chief Scientist Office of Naval Research 1030 East Green Street Pasadena, California	1
Dr. T. L. Brownyard Bureau of Naval Weapons Department of the Navy Attn: Code RRE-5 Washington 25, D.C.	1
Dr. E. E. Gruber Head, Plastics Research General Tire & Rubber Co. Research Laboratory Akron, Ohio	1

Sheet 1 of 2

**UNCLASSIFIED**

**UNCLASSIFIED**

Report No. 0235-01-22

DISTRIBUTION LIST (cont.)

No. of Copies

Stanford Research Institute  
Menlo Park, California  
Attn: Marion Hill

1

CPIA List as required

27

Internal

Sheet 2 of 2

**UNCLASSIFIED**